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by

Walter M. Shackelford and John M. McGuire
Environmental Research Laboratory
U.S. Environmental Protection Agency
Athens, GA 30613

ENVIRONMENTAL RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
ATHENS, GA 30613

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16. ABSTRACT

The development of the present methodology for the analysis of extractable priority pollutants in water is presented. The methodology offers high selectivity, sensitivity, and cost effectiveness through the use of gas chromatography-mass spectrometry-computer system. Confidence in the method in wastewater is backed by a 15-laboratory validation study. Quality control procedures required by the method offer adequate assurance while using minimal resources.

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Walter M. Shackelford and John M. McGuire

U.S. Environmental Protection Agency

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Athens, Georgia 30613

Following the June 1976 Consent Decree (NRDC et al. vs. EPA), there has been a continuously increasing demand for the analysis of water samples for the 129 priority pollutants. The protocol originally designed for the analysis of the priority pollutants that are extractable into dichloromethane has been refined to take advantage both of increased experience by analytical chemists and improvements in laboratory instrumentation and automation. Quality control procedures have been set forth that are designed to insure top quality laboratory performance and establish confidence in the reliability of results over a wide range of sample matrices. This paper follows the development of present methodology for the analysis of extractable priority pollutants in water.

Compounds Analyzed. The specific compounds to be analyzed are found in Table 1 (acids) and Table 2 (base/neutrals and pesticides).

Table 1. Acid Extractable Priority Pollutants

Compound Name	Chemical Abstracts Registry No. (CASRN)
4-Chloro-3-methylphenol	59-50-7
2-Chlorophenol	95-57-8
2,4-Dichlorophenol	120-83-2
2-Methyl-4,6-dinitrophenol	534-52-1
2-Nitrophenol	88-75-5
4-Nitrophenol	100-02-7
Pentachlorophenol	87-86-5
Phenol	108-95-2
2,4,6-Trichlorophenol	88-06-2

Table 2. Base/Neutral and Pesticide Extractable Priority Pollutants

Compound Name	Chemical Abstracts Registry No. (CASRN)
Acenaphthene	83-32-9
Acenaphthylene	208-96-8
Anthracene	120-12-7
Aldrin	309-00-2
Benzo(a)anthracene	56-55-3
Benzo(b)fluoranthene	205-99-2
Benzo(k)fluoranthene	207-08-9
Benzo(a)pyrene	50-32-8
Benzo(ghi)perylene	191-24-2
Benzyl butyl phthalate	85-68-7
β-BHC	319-85-7

Table 2. Base/Neutral and Pesticide Extractable Priority Pollutants (Continued)

Compound Name	Chemical Abstracts Registry No. (CASRN)
δ-BHC	319-86-8
Bis(2-chloroethyl)ether	111-44-4
Bis(2-chloroethoxy)methane	111-91-1
Bis(2-ethylhexyl)phthalate	117-81-7
Bis(2-chloroisopropyl)ether	108-60-1
4-Bromophenyl phenyl ether	101-55-3
Chlordane	57-74-6
2-Chloronaphthalene	91-58-7
4-Chlorophenyl phenyl ether	7005-72-3
Chrysene	218-01-9
4,4'-DDD	72-54-8
4,4'-DDE	72-55-9
4,4'-DDT	50-29-3
Dibenzo(a,h)anthracene	53-70-3
Di-n-butylphthalate	84-74-2
1,3-Dichlorobenzene	541-73-1
1,2-Dichlorobenzene	95-50-1
1,4-Dichlorobenzene	106-46-7
3,3'-Dichlorobenzidine	91-94-1
Dieldrin	60-57-1
Diethyl phthalate	84-66-2
Dimethyl phthalate	131-11-3
2,4-Dinitrotoluene	121-14-2
2,6-Dinitrotoluene	606-20-2

Table 2. Base/Neutral and Pesticide Extractable Priority Pollutants (Continued)

Compound Name	Chemical Abstracts Registry No. (CASRN)
Di-n-octylphthalate	117-84-0
Endosulfan sulfate	1031-07-8
Endrin aldehyde	7421-93-4
Fluoranthene	206-44-0
Fluorene	86-73-7
Heptachlor	76-44-8
Heptachlor epoxide	1024-57-3
Hexachlorobenzene	118-74-1
Hexachlorobutadiene	87-68-3
Hexachlorocylopentadiene	77-47-4
Hexachloroethane	67-72-1
Indeno(1,2,3-cd)pyrene	193-39-5
Isophorone	78-59-1
Naphthalene	91-20-3
Nitrobenzene	98-95-3
N-Nitrosodimethylamine	62-75-9
N-Nitrosodiphenylamine	86-30-6
N-Nitrosodi-n-propylamine	621-64-7
PCB-1016	12674-11-2
PCB-1221	11104-28-2
PCB-1232	11141-16-5
PCB-1242	53496-21-9
PCB-1248	12672-29-6
PCB-1254	11097-69-1

Table 2. Base/Neutral and Pesticide Extractable Priority Pollutants (Continued)

Compound Name	Chemical Abstracts Registry No. (CASRN)
PCB-1260	11096-82-5
Phenanthrene	85-01-8
Pyrene	129-00-0
Toxaphene	8001-35-2
1,2,4-Trichlorobenzene	120-82-1
Benzidine	92-87-5
α-BHC	319-84-6
γ-BHC	58-89-8
Endosulfan I	959-98-8
Endosulfan II	33213-65-9
Endrin	72-20-8

Method Description. The detailed procedures for analysis of the extractable priority pollutants are called Method 625 and may be found elsewhere (1,2). The method consists of extraction of the organics into methylene chloride, drying of the extract by passing it through a sodium sulfate column, concentration of the extract by Kuderna-Danish evaporation, and analysis of the concentrate by GC/MS. In Figure 1 a flow diagram depicts the steps of the analysis scheme.

This procedure essentially follows the classical GC analysis schemes for pesticides in water with a few notable exceptions. First, allowance is made for compounds that may be ionized in more or less neutral (pH 5-9) aqueous solutions by requiring two consecutive pH-adjusted extractions. Second, the detector employed is a mass spectrometer. Finally, no clean-up procedure is

called for, because sample compounds not on the priority pollutant list (3,4) that could be lost in a clean-up step may also be of interest.

The fact that interfering compounds are expected to be present and the fact that these compounds may constitute a data resource requires the use of a detector that offers considerably more qualitative information than conventional flame ionization, electron capture, or halogen selective detectors. The mass spectrometer provides such qualitative selectivity at a sensitivity that is necessary for the analysis of treated wastewater. The method calls for identification of priority pollutants by matching three characteristic masses (m/z) of each compound with those of standards and the retention time of the compound with the appropriate standard within $\pm$ 30 seconds on a packed GC column.

Quantitative analysis of the extractable organics is accomplished by the use of internal standards. The recommended standards are primarily isotope-labelled (deuterated) analogs of the priority pollutants themselves. Labelled internal standards have the obvious advantage in MS analyses of behaving much the same chromatographically as their natural analog yet usually being mass resolved. Thus, the internal standard does not interfere with qualitative analysis.

Allowance is made in the method for use of chromatographic columns different from those specified in the method. Additionally, the use of continuous liquid-liquid extraction is recommended for samples that produce emulsions during shake-out extractions. The flexibility accorded by these two allowances enhances the laboratory's ability to deal with the many difficulties arising from a wide range of sample matrices. The results of a 15-laboratory method validation study (5) are given in the method to allow each laboratory to compare its precision and recovery data to those of the validation. The confidence

limits defined by the validation study determine the acceptability of each laboratory's performance.

Development of the Method. As has been stated in another paper in this series (6), EPA was required by court order in 1976 to prescribe the Best Available Treatment (BAT) for wastewater in 21 industrial categories. To determine the efficacy of treatment technologies, analysis of both influent to treatment and effluent waters had to be performed. Thus, the analysis protocol had to be able to establish the presence of the priority pollutants in a wide variety of matrices, in the presence of many closely related compounds, and within greatly varying concentration ranges.

Referring to Tables 1-2, one can infer the range of compound polarities, molecular weights, and aqueous solubilities that will affect any general analysis scheme designed to determine all of these compounds in any given sample. Likewise, the number of target compounds coupled with the probable number of interfering compounds in an industrial waste affects the choice of a detector.

From the outset, it was obvious that gas chromatography coupled with computerized mass spectrometry (GC/MS/COM) would be the only instrumental technique capable of handling the interference problems that could be foreseen. (It also has handled many of the originally unforeseen problems.) An additional benefit that was recognized was the ability of GC/MS/COM to acquire data for both target compounds and other compounds so that if other compounds became important, the data could be reanalyzed for them without acquiring new samples. Although the cost of the mass spectrometer was at least one order of magnitude greater than the common GC detectors, the costs of sample analyses if many compounds were to be sought was shown actually to be cheaper using the mass spectrometer as a detector (7).

The choice of using the mass spectrometer for a detector for water pollutants led to a spectacular rise in its routine use in the Agency. In 1971, EPA committed itself to the purchase of more than 20 GC/MS/COM systems for its laboratories (8). A report on then-current practices of analysis of organics in water issued in 1973 (9) by the Agency listed over 200 compounds tentatively identified in water using dichloromethane extraction, Kuderna-Danish concentration, and GC/MS/COM analysis. A 1975 review of applications of mass spectrometry in environmental analysis during 1969-1974 lists 396 papers with 25 studies on the characterization of industrial wastewaters (10). The same reviewer listed 274 papers in the year 1975 alone in a 1977 review (11) with 10 papers on industrial wastewater analysis. By 1976, over 1200 organics had been identified in waters of all types by GC/MS/COM (12).

EPA, however, was not alone in its use of GC/MS/COM techniques in water analysis. A symposium on the "Identification and Analysis of Organic Pollutants in Water" at the First Chemical Congress of the North American Continent in Mexico City in December 1975 contained papers on GC/MS/COM of water samples from academic, industrial, and governmental sources (13). In fact, the hallmark of the successful applications of these techniques to wastewater analysis has always been the cooperation of interested scientists in the field from all backgrounds.

It is obvious from the above discussion that the original protocol for analysis of the extractable priority pollutants was preceded by fragmented efforts from many researchers. When the call came to develop a protocol for analysis of these compounds, even though the deadline was only a few months ahead, there was ample precedent for the decisions that were made.

EPA's Effluent Guideline Division in the Office of Water had responsibility for developing the effluent regulations while the Office of Research and

Development's (ORD) Environmental Monitoring and Support Laboratory in Cincinnati was given overall responsibility for producing the protocol for analysis of the priority pollutants. ORD's Environmental Research Laboratory in Athens was given responsibility for developing the extractable analysis protocol. Since the Effluent Guidelines Division already had contracts in place with Midwest Research Institute and Environmental Science and Engineering for analysis of the tanning and wood products industries, these two laboratories tested early versions of the protocol and added knowledge gained from field sample experience. A meeting of the American Society for Testing and Materials' Committee D-19.06 in Cincinnati in early 1977 enabled scientists from the regulated industries to input their experiences to the genesis of the protocol.

There also were constraints to be considered that had nothing to do with detectors or sample matrices. Samples were to be analyzed by contract laboratories selected through an invitation for bid. This meant that once a group of laboratories qualified for the bidding, no consideration other than price could be made for selection of a contractor. Development of the protocol, then, required development of a list of bidder qualifications to eliminate potential bidders who lacked the expertise or equipment to accomplish the analysis.

As published in March 1977 (revised April 1977) (14), the original analysis protocol contained a few firsts for a routine analysis scheme. A computer was required for both instrument control and data reduction. Identification of the compounds of interest was to be accomplished by matching a few characteristic ions (three) of the suspected pollutant with those of the proper standard, and the ions had to simultaneously peak within a $\pm$ 1 min retention time window that was determined by standards. All raw data had to be archived on 9-track magnetic tape and provided as a contract deliverable. Finally, to demonstrate proper system operation before sample analysis, the compound decafluorotriphenyl-

phosphine (DFTPP) had to be chromatographed and detected at the 20 ng level. Moreover, the DFTPP spectrum had to be consistent with that published by Eichelberger et al. (15).

In the early phases of protocol development, it was suggested that one GC column be used for all extractable compounds. This idea, although since realized after the advent of fused silica capillary columns, had to be abandoned at the time because of the range of polarities of the extractable compounds. It was possible to get by with only two columns, however. A medium polarity liquid phase, SP-2250 (50% methyl, 50% phenyl silicone), was chosen after evaluation of several similar phases for the base/neutral fraction. Initially, Tenax GC was chosen for the acid fraction. Within a year, however, the development of SP-1240 DA (polyester) led to the replacement of Tenax GC with SP-1240 DA (16). Both SP-2250 and SP-1240 DA remain the recommended column packings in the latest revision of Method 625 (1).

In the original protocol, quality control was limited to insuring that the instrumentation was operating properly. In developing the protocol, it had been noted that column performance could be monitored by observing the chromatography of benzidine on the base/neutral column and pentachlorophenol on the acid column. It was specified that both of these compounds had to be chromatographed successfully before analysis could take place. Mass spectrometer tune and sensitivity was to be monitored by the analysis of a DFTPP standard as mentioned above. Although these system checks remain in Method 625 today, the quality control measures have become vastly more comprehensive.

Fine tuning of the method began almost immediately. In November 1977 the first of a still-continuing series of symposia on analytical methods for priority pollutants was held. The purpose then as now was strictly to allow the interchange of problems and ideas on the analysis of priority pollutants. Industrial,

contractor, and agency scientists participated in the meetings. In June 1978 ASTM (17) held a symposium in Denver to define the state of the art in water analysis. At this meeting representatives of industrial groups stressed the need for validation of the method.

Validation studies began with the implementation of a quality control program directed by the EMSL-Cincinnati. At the 1978 and 1979 analytical method symposia the requirements of the quality control program (18) and the outline of a validation program (19) were laid out.

At the end of 1979, Method 625 was published in the Federal Register for public comment (20). Several persuasive ideas came from the public comment procedure that were made part of successive revisions. The need for an interlab validation study was expressed by many commenters. Flexibility in GC column choices, solvent evaporation techniques, and extraction techniques (batch or continuous) was recommended also. Meanwhile, the use of fused silica capillary columns was applied to the extractable priority pollutants, chromatographing both acidic and base/neutral fractions on the same column (21) and later even the volatile fraction (22). In a precision and accuracy comparison of packed and fused silica capillary columns, it was shown that recovery values were greater overall using the fused silica columns (23).

Most of the persuasive comments and options to allow the new column technology were incorporated in the method by the EMSL-Cincinnati in an EPA report in July 1982 (2). With the completion of the validation study (5), the final version of Method 625 was published in the Federal Register (1) in October 1984.

Quality Control. As mentioned above, the quality control measures recommended in the original protocol were vestigial at best. As the method was published for public comment (20), the quality control procedures were

suggested but were not yet a required part of the method. An appendix to the method gave recommended procedures for recovery studies, validation of the method for each sample matrix encountered, and ongoing quality control. The concept of using surrogate standards, surrogates being compounds spiked in the actual sample that were known not to be sample components, was initiated in this quality control program. The use of surrogate standards allowed a quality control check on each sample, while limiting the total number of samples run for quality control purposes alone. Although an example of a validation study was given as an appendix to the recommended QC procedures, no actual validation data were given and no validation standards were available.

By the July 1982 revision of the method (2), however, the recommended QC procedures had now become a mandatory part of Method 625. In addition, method performance criteria such as method detection limit (24) and multi-lab precision and accuracy data were available for aiding the judging of laboratory performance. The EMSL-Cincinnati also announced the availablity of quality control check samples at this time. Surrogate and internal standards were given in a list of deuterated and fluorinated compounds, many of which were analogous to the priority pollutants.

The latest revision (1) of Method 625 includes the results of the 15-lab validation study. In order to perform the method successfully, the laboratory must generate data that fall within established performance criteria that were generated in the validation (5). To insure that the check samples are uniform, the laboratory is instructed to obtain them from the EMSL-Cincinnati if available. Laboratories are instructed to spike at least 5% of all samples from each sampling site as a part of ongoing QC. Table 4 details the steps in the required QC procedure.

Table 4. Required Quality Control

I. Reagent water blank.

A. Demonstrates that the analytical system and glassware interferences are under control.

B. Must be demonstrated with each new set of samples or new lot of reagents.

II. Initial precision and accuracy study.

A. QC check sample concentrate is obtained from EMSL-Cincinnati.

B. Four replicates of reagent water are spiked at the 100 ppb level with all extractable priority pollutants.

C. Precision and accuracy data must meet acceptance criteria given in the method.

D. Study must be repeated for any parameters that do not meet the acceptance criteria.

III. Ongoing matrix spike study.

A. At least 5% of all samples from a sampling site must be spiked.

B. Spike with the QC check sample concentrate.

C. Compare precision and accuracy data with acceptance criteria given in the method.

D. If a parameter fails the acceptance criteria, prepare a QC check sample in reagent water to test performance.

IV. Surrogate standard spike.

A. All samples must be spiked with surrogate standards.

B. Calculate and record recovery of each surrogate.

Conclusions. Analysis of extractable priority pollutants is aided greatly by the application of EPA's Method 625. The method offers high selectivity, sensitivity, and cost effectiveness through the use of GC/MS/COM. Confidence in the method in wastewater is backed up by a 15-laboratory validation study. Quality control procedures that are required by the method offer adequate assurance while using minimal resources.

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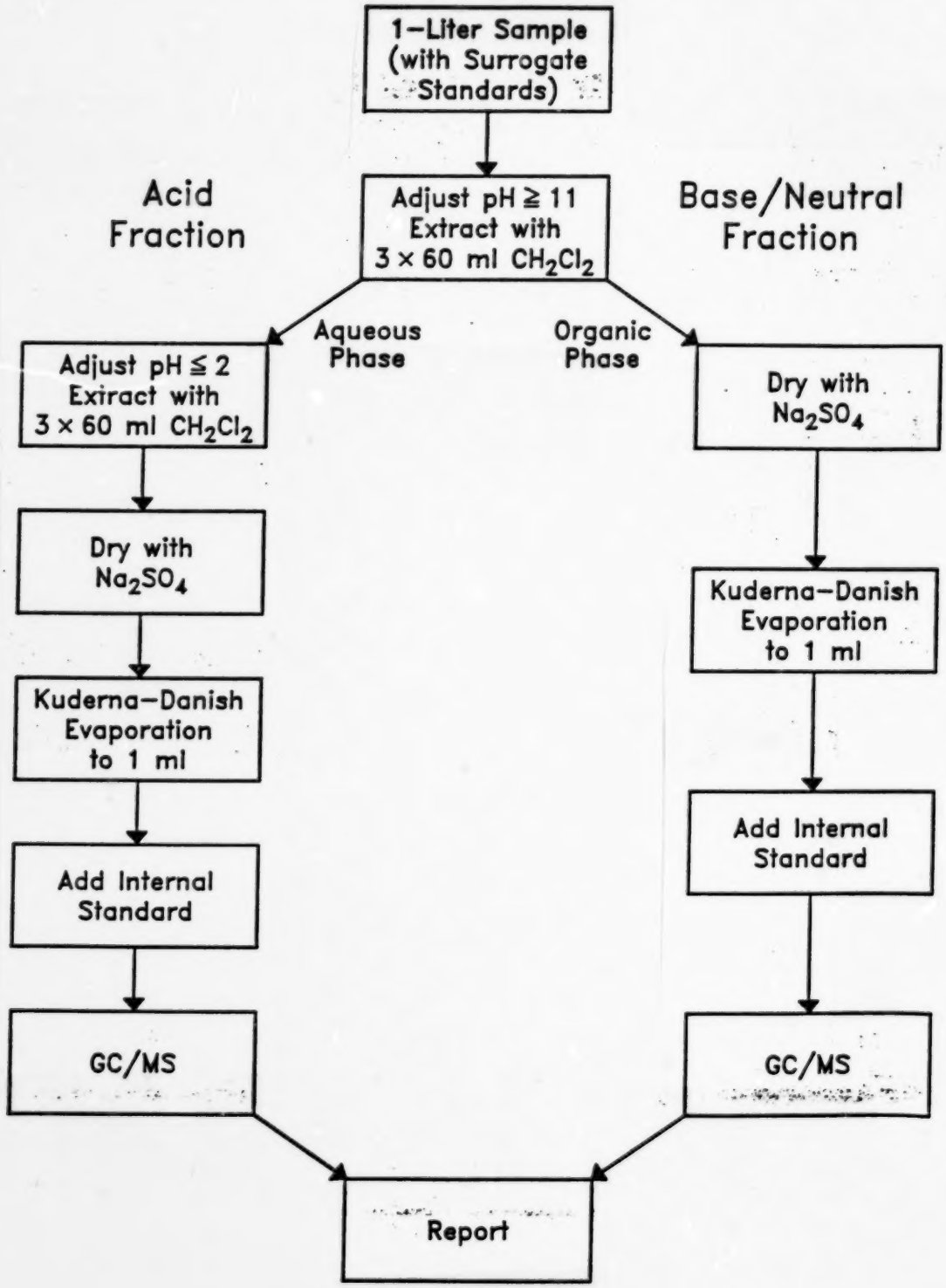
1-Liter Sample (with Surrogate Standards)
Adjust pH ≥ 11 Extract with 3 × 60 ml CH_2Cl_2
Acid Fraction
Base/Neutral Fraction
Aqueous Phase
Organic Phase
Adjust pH ≤ 2 Extract with 3 × 60 ml CH_2Cl_2
Dry with Na_2SO_4
Kuderna-Danish Evaporation to 1 ml
Add Internal Standard
GC/MS
Dry with Na_2SO_4
Kuderna-Danish Evaporation to 1 ml
Add Internal Standard
GC/MS
Report